Thermodynamic Properties of the Spin-1/2 Antiferromagnetic ladder $Cu_2(C_2H_{12}N_2)_2Cl_4$ under Magnetic Field

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Specific heat (C_V) measurements in the spin-1/2 $Cu_2(C_2H_{12}N_2)_2Cl_4$ system under a magnetic field up to $H = 8.25T$ are reported and compared to the results of numerical calculations based on the 2-leg antiferromagnetic Heisenberg ladder. While the temperature dependences of both the susceptibility and the low field specific heat are accurately reproduced by this model, deviations are observed below the critical field H_{C1} at which the spin gap closes. In this Quantum High Field phase, the contribution of the low-energy quantum fluctuations are stronger than in the Heisenberg ladder model. We argue that this enhancement can be attributed to dynamical lattice fluctuations. Finally, we show that such a Heisenberg ladder, for $H > H_{C1}$, is unstable, when coupled to the 3D lattice, against a lattice distortion. These results provide an alternative explanation for the observed low temperature ($T_C \sim 0.5K - 0.8K$) phase (previously interpreted as a 3D magnetic ordering) as a new type of incommensurate gapped state.

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Wide interest is currently devoted to "gapped" spin systems, both experimentally and theoretically. In one dimension, $S = 1$ Haldane and alternating spin chains provide good examples of such systems. When magnetic frustration is present, similar situations can be found not only in one-dimension (1D) – the $J_1 - J_2$ model for instance – but also in two (2D) or three dimensions. An intermediate situation between 1D and 2D is provided by the so-called "ladder" systems, which couple an even number of quantum spin ($S = 1/2$) chains. As for alternating and frustrated spin chains, the energy diagram is characterized by an energy gap Δ_S between the $S = 0$ ground state (GS) and the first magnetic $S = 1$ excited state leading to characteristic magnetic and thermodynamic properties at low enough temperature, $T < \Delta_S$.

The application of a magnetic field yields drastic changes in the energy spectrum. In particular, as a result of the Zeeman splitting undergone by the $S = 1$ excited state, a second-order transition occurs at the critical field $H_{C1} = \Delta_S/g\mu_B$, where g is the gyromagnetic ratio and μ_B the Bohr magneton. Above H_{C1}, the GS becomes magnetic [1] and a continuum of excitations develops giving rise to "incommensurate" zero-energy fluctuations.

Experimentally, the study of such a Quantum High Field (QHF) phase, i.e. for $H > H_{C1}$, requires to work on systems having a relatively small gap Δ_S. Indeed, insulating ladders such as $SrCu_2O_3$ [2] whose structure is closely related to the parent 2-dimensional cuprate antiferromagnets typically have spin gaps larger than $100K$. This explains that such a phase has rarely been investigated. As shown by recent studies, an interesting opportunity is provided by the compound $Cu_2(C_2H_{12}N_2)_2Cl_4$ (also known as CuHpCl) which is thought to behave as an ideal 2-leg spin-1/2 ladder system with a critical field of $H_{C1} \simeq 7.5T$. Magnetic measurements have been used first to characterize the magnetic parameters of the spin system. The behavior of the magnetic susceptibility, reproduced from Refs. [3,4] in Fig. 1, is consistent with a gap of the order of $\Delta_S \sim 11K$. Specific heat (C_V) measurements in CuHpCl have recently been performed under a magnetic field of up to $9T$ [5]. In low field ($H < H_{C1}$), a single maximum is observed at relatively high temperature ($T \sim J_\perp$), and, due to the presence of the energy gap, C_V decreases exponentially at low temperature [$\sim \exp(-\Delta_S/T)$]. In addition, a second order transition was shown to occur at very low temperature ($0.5K < T_C < 0.8K$) and was interpreted as the onset of 3-dimensional (3D) magnetic order.

In the present work, new specific heat measurements in a field (up to $8.25T$) are presented which mainly focus on the QHF phase. They were performed by using a scanning adiabatic method. A small known power is applied to a high purity silicon sample holder and the temperature difference between the sample and a surrounding radiation screen is measured by a gold-iron thermocouple using a DC squid device as a current amplifier. A feedback network maintains the radiation screen at the same temperature as the sample, then strongly reducing the heat exchange process. The temperature rises slowly from 0.1 K to 8K, at a speed as slow as 10 mK/min. The

measurement of the temperature of the radiation screen then allows the specific heat of the sample to be calculated. Such a slow drift rate in temperature ensures that all parts of the sample are in thermal equilibrium, and unlike pulsed methods the specific heat of non metallic materials with poor thermal diffusivities can be accurately measured. In the present work, four single crystals glued onto a mica plate (as in previous susceptibility experiments [3,4]) were measured. Each crystal weighed approximately 0.5 mg. The contributions of all the addenda - the mica , varnish, vacuum grease, and the silicon sample holder - were estimated and subtracted. The behaviors observed are directly compared to the results of a numerical investigation based on the Heisenberg ladder model. In the QHF phase, a second maximum develops at low temperature. Above T_C, we observed deviations from the isolated ladder model (the contribution of the low energy "incommensurate" spin fluctuations occurs at larger fields) which, we argue, can be due to dynamical lattice fluctuations. We suggest an alternative explanation for the low temperature phase in terms of a new incommensurate gapped state. A calculation based on a Heisenberg ladder coupled to 3D (classical) phonons strongly supports this scenario.

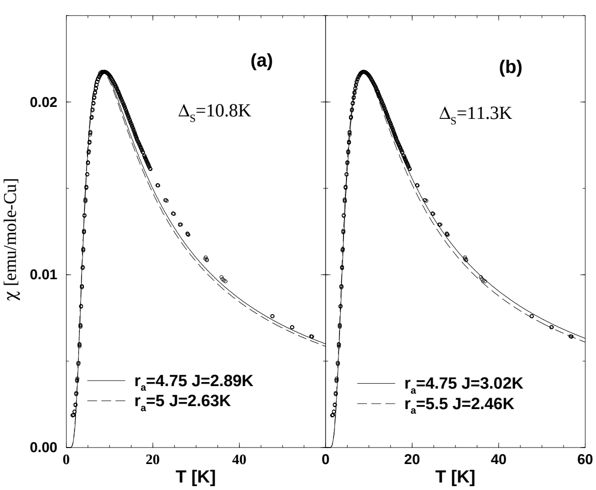

FIG. 1. Theoretical fit of the temperature dependence of the magnetic susceptibility. The experimental data are taken from Refs. [3,4]. The anisotropy ratios $r_a = J_\perp / J_\parallel$ as well as the magnetic coupling along the chain $J = J_\parallel$ are indicated on the plots. (a) and (b) correspond to various set of parameters producing two different spin gaps Δ_S.

The Hamiltonian we shall use to describe the compound is the Heisenberg model on a ladder defined by

$$\mathcal{H} = J_\perp \sum_j \mathbf{S}_{j,1} \cdot \mathbf{S}_{j,2} + J_\parallel \sum_{\beta,j} \mathbf{S}_{j,\beta} \cdot \mathbf{S}_{j+1,\beta} \tag{1}$$

where β (=1,2) labels the two legs of the ladder (oriented along the x-axis), j is a rung index (j=1,...,L) and $J_\parallel$ and $J_\perp$ are the bond strengths along and between the chains respectively. An applied field H in the Z-direction leads to an additional Zeeman term, $\mathcal{H}_Z = -g\mu_B H \sum_{\beta,j} S^Z_{j,\beta}$, with an average value $g \simeq 2.08$ [4].

Our numerical approach is based on Exact Diagonalisation techniques. At $T = 0$, clusters with size up to 2×14 can be handled with the Lanczos algorithm allowing, after a proper finite size scaling procedure, for accurate determinations of the various physical quantities [8]. At finite temperature, a full diagonalization of 2×6, 2×8 and 2×10 ladders has been performed. According to previous literature, the anisotropy ratio $r_a = J_\perp / J_\parallel$ lies around 5. In this regime, the spin correlation length is smaller than the system sizes so that finite size corrections become negligable.

In order to test the choice of parameters in (1), let us briefly consider the temperature dependence of the magnetic susceptibility [4]. A comparison between the numerical and the experimental data is shown in Fig. 1. In fact, the quality of the fit is not very sensitive to the anisotropy ratio (in the range $4.75 \le r_a \le 5.5$). Parameters producing a gap of $\Delta_S \simeq 10.8K$ (as reported in Ref. [4]) or $\Delta_S \simeq 11.3$ (as reported in Ref. [6]) give excellent fits of the experimental data. As shown numerically [7] or in a strong coupling approximation [6] the experimental behavior of the magnetization vs H is well reproduced by a similar set of parameters.

Concerning the specific heat measurements shown in Figs. 2, the exponential behavior at low temperature characteristic of the spin gap is suppressed at moderate magnetic fields. Above $7.5T$, a broad maximum in $C_V(T)$ builds up signaling the emergence of new low energy fluctuations [10]. The numerical calculations of $C_V(T)$ in Fig. 2(b) based on the above ladder model (with parameters leading to $H_{C1} \simeq 7.7T$) reveal qualitatively the same behavior. At low field, up to $H = 6T$, the agreement with experiment is very good, hence establishing the relevance of the ladder model (1) in this regime. In the QHF, however, the maximum observed in the theoretical calculation appears at higher magnetic fields than in experiment. Deviations from the theoretical behavior appear at low temperature for fields above $7.5T$ after the closing of the ladder gap. We argue here that this effect can be due to lattice fluctuations. In fact, it has been shown [11] for uniform Heisenberg chains, in the context of spin-Peierls transitions, that an underlying spin-lattice coupling can lead to significant deviations e.g. in the magnetic susceptibility which can be accounted for by an effective exchange coupling. As shown in Fig. 2(c), a behavior qualitatively similar to the experimental observations can be obtained by using renormalized exchange couplings $J^{\rm eff}_\mu = c\, J_\mu$ ($\mu = \perp, \parallel$), $c \le 1$, which, according to Ref. [11], is consistent with the effect of a coupling to the lattice. For increasing field above $7T$, the renormalization parameter c decreases signaling an increasing role played by the lattice coupling.

Motivated by the above discussion, we reasonably assume the presence of a magneto-elastic coupling along

the chain direction [12] by replacing the second term of Eq. (1) by

$$\mathcal{H}_{\parallel} = J_{\parallel} \sum_{\beta,j} (1+\delta_{\beta,j}) \mathbf{S}_{j,\beta} \cdot \mathbf{S}_{j+1,\beta} + \frac{1}{2} K \sum_{\beta,j} \delta_{\beta,j}^2 \,, \quad (2)$$

where the second term corresponds to the (3D) lattice elastic energy and where the set of parameters $\{\delta_{\beta,j}\}$ (proportional to the atomic displacements) have to be determined by minimizing the total energy.

Hamiltonian (2) can lead to a lattice distortion (i.e. that $\{\delta_{\beta,j}\} \neq 0$) in the strong coupling limit i.e. when $J_{\perp} \gg J_{\parallel}$. In this case, for $H \geq H_{C1}$, by retaining the $S^Z = 1$ and $S^Z = 0$ states only on each rung (see e.g. [6,13]), the spin ladder reduces to a 1D spinless fermion model [14] with a hopping amplitude $t = J_{\parallel}/2$ and a nearest neighbor repulsion $V = J_{\parallel}/2$. Physically, a particle corresponds, in the original spin language, to a $S_Z = 1$ rung triplet excitation so that the effective band filling is directly proportional to the relative magnetization $M/M_{\rm sat}$ in such a way that $2k_F = 2\pi(M/M_{\rm sat})$. If one neglects the short range repulsion V between the particles (this should be justified for low particle density i.e. small magnetization), as in the usual Peierls transition, a modulation of the hopping amplitude $t = J_{\parallel}/2$ of wavevector $2k_F$ and magnitude δ opens a gap at the chemical potential and leads to an energy gain $\Delta E \propto \delta^2 \ln(\text{const}/\delta)$, for $\delta \ll 1$. For arbitrary large K, the minimum of the total energy is then obtained for an equilibrium value $\delta \sim \exp(-\text{const}K)$.

In order to explore the relevance of the previous scenario, a numerical investigation on finite clusters is required. The following study has been restricted to $T = 0$ and simple ratios for $M/M_{\rm sat}$ like 1/3, 1/2 or 2/3. The minimization of the total energy using expression (2) can be realized by an Exact Diagonalization technique supplemented by a self-consistent procedure [15]. A typical GS configuration is shown in Fig. 3(a) for a magnetization $M = \frac{2}{3} M_{\rm sat}$. The lowest energy is obtained for a perfectly symmetric modulation of the two chains i.e. $\delta_{\beta,j} = \delta_j$. The variation of the distortion δ_j along the ladder is correlated with that of the spin density and is a periodic function of period $\lambda_F = M_{\rm sat}/M$. For the special case $M/M_{\rm sat} = 1/2$, the distortion becomes commensurate and corresponds to a simple dimerization of the lattice, similar to the D-phase observed in spin-Peierls chains such as $\mathrm{CuGeO_3}$ in the *absence* of a magnetic field.

In order to study the stability of these modulated phases we have defined a critical elastic constant as $K_C = \lim_{|\delta_j| \to 0} \{\Delta E / \sum_j \delta_j^2\}$, where ΔE corresponds to the magnetic energy gain due to the equilibrium distortion pattern. The distorted phase is then stable for $K \leq K_C$. Our results displayed in Fig. 3(b) as a function of the ratio $J_{\perp}/J_{\parallel}$ show that K_C increases with system size; although it is difficult to extrapolate our results to the thermodynamic limit, they clearly establish that a small spin-lattice coupling leads to modulated structures. It is interesting to notice that, for a small $M/M_{\rm sat}$

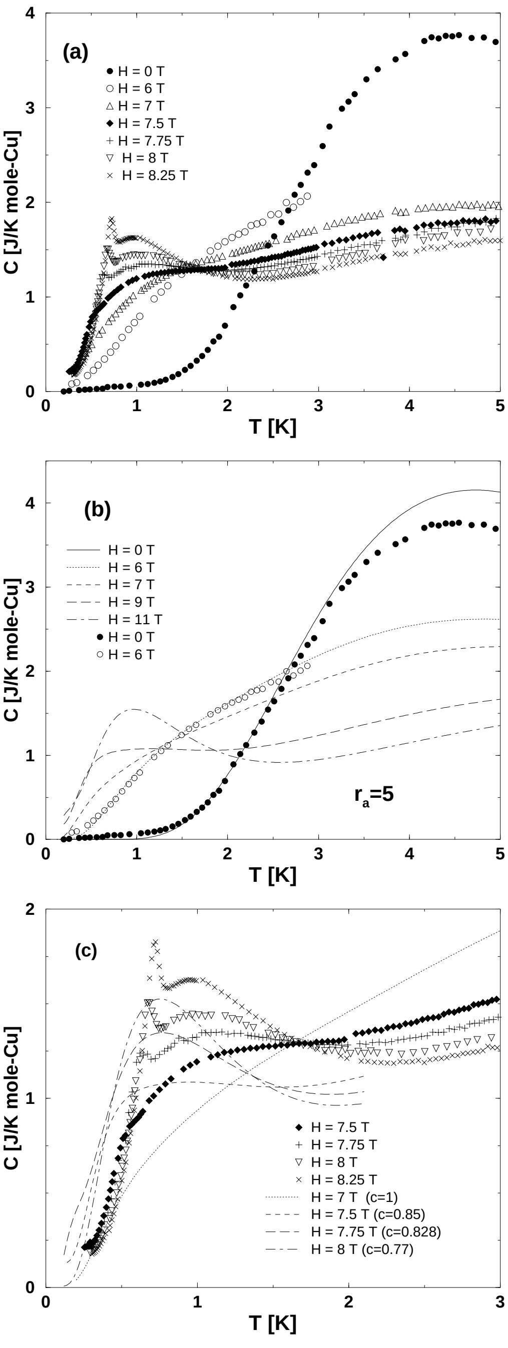

FIG. 2. Specific heat vs T for different values of the magnetic field. (a) Experimental data. (b,c) Comparison between experiment (symbols) and theory (lines) using $r_a = 5$, $J_{\parallel} = 2.63K$.

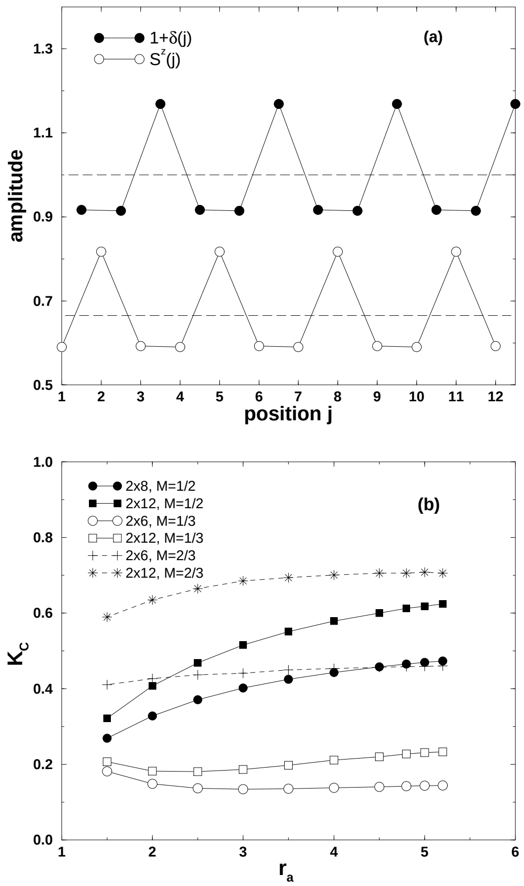

FIG. 3. (a) Equilibrium modulation $1+\delta_j$ and corresponding average spin density $\langle (S^Z_{j,1}+S^Z_{j,2}) \rangle$ vs the position along the ladder direction calculated on a 2×12 cluster for $r_a = 5$, $K = 0.6$ and $M/M_{\rm sat} = 2/3$. (b) Critical value K_C as a function of the anisotropy ratio $r_a = J_\perp/J_\parallel$ for $M/M_{\rm sat} = 1/3$, 1/2 and 2/3. The system sizes are indicated on the plot.

(i.e. for H just above H_{C1}), a simple $2k_F$ modulation is expected (in this regime, the short range repulsion V becomes irrelevant) while, for $M/M_{\rm sat}$ close to 1/2 more complicated incommensurate structures of "soliton lattice" type (i.e. involving an infinite number of higher harmonics) [16] should be stabilized. All these incommensurate structures bear strong similarities with the I-phase of the spin-Peierls systems [15] and have similar properties as e.g. the existence of a gap [17].

To conclude, we have shown that the specific heat data for $H \leq H_{C1}$ are quantitatively well described by an isolated Heisenberg ladder model. Deviations from the predictions of this model observed for $H > H_{C1}$ and low temperatures are attributed to the effect of a small magneto-elastic coupling to the 3D lattice. We have shown numerically that, in this regime, the Heisenberg ladder becomes unstable against a lattice distortion leading to a new gapped incommensurate phase.

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